Stable Cu and Zn isotopes as tracers of contamination in organic waste-amended soils.

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Agriculture, and particularly animal husbandry, is one of the major waste producing activities on the planet. In response to continuously growing demand for animal protein, livestock production generates increasing amounts of manure. In 2017, 1 billion pigs were produced in the World, with approximately half of it in China. Livestock manure treatment and disposal have become a major issue of the present-day agriculture. Spreading this organic-rich amendment on the soil helps improving soil physico-chemical properties and fertility at the same time that allows the manure recycling. Yet, pig and dairy manures are also rich in Cu and Zn. These potentially toxic trace metals are added to the animal feed, but not digested by the animals. Thus, intensive use of pig and dairy manures as amendment has for a consequence massif inputs of Cu and Zn in agricultural soils.

In order to anticipate and prevent degradation of agricultural soils amended with livestock manure, it is crucial to understand the sources and the long-term behavior of these exogenous metals. Published works on manure-borne Cu and Zn in soils described rather low plant uptake, contamination of water resources and accumulation within the soil. A few studies, focused on the speciation, showed that Cu and Zn are present as Cu_2S and ZnS in the pig manure. However, no ZnS was detected in soils amended with pig slurry, instead, Zn was found to be adsorbed on clay minerals and iron ox-hydroxides. In addition, none of these studies was able to differentiate between natural and exogenous trace elements.

We have investigated manure-amended soils and the corresponding pig and dairy manures applied over several years in three experimental sites located in Brazil. We have analyzed Cu and Zn concentrations and isotopic compositions aiming at evaluating the potential of stable Cu and Zn isotopes as tracers of exogenous metal transformation and redistribution in soils. We observed that livestock manure amendments have rather homogeneous Zn isotopic compositions but show differences in Cu isotopic compositions, depending on the type of waste (pig slurry or dairy manure). Furthermore, Cu and Zn isotopic compositions of the soils that have received large amounts of manure amendments are (i) different from those of the control soil and (ii) intermediate between the isotopic compositions of the control soil and the manure applied. Thus, although the original isotopic signature of a given manure is most likely modified after spreading on the soil, the input of manure-borne Cu and Zn can be detected in soils, particularly in the case of massive treatments. These preliminary results show that stable Cu and Zn isotopes represent a promising tool for studying the behavior of exogenous trace elements from organic-rich amendments. Further application of this approach opens new perspectives, particularly for investigating target mineral phases and long-term behavior of these metal in soils, as well as for tracing the source of contamination in areas without monitoring history.